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19. ABSTRACT (Continue on reverse if necessary and identify by block numbers) It is well known that the characteristics of hydrated calcium aluminosilicate materials (macrodefect-free, silica-enriched cement) are directly related to the bulk composition of the starting materials which dictate the phases developing during the hydration process. Although countless examples of this empirical relationship can be found in the literature, very little in terms of a systematic study of phase, morphology, and intrinsic property relations are actually available. At this time, seven glasses will serve as simplified starting materials for ongoing solution and paste hydration studies. The experiments will provide insight into kinetics of reaction, phase development and microstructure paralleling that which occurs in high-strength construction materials such as structural concrete and other less traditional chemically bonded ceramics. Our objective is to begin to understand the nature of microstructure, porosity and mechanical property relationships of calcium silicate hydrate and its coexisting phases. By delineating phase relations among (over)			
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these largely amorphous, gel-like materials it may then be possible to engineer these materials for a variety of purposes. For example, using simple hydration and low temperature processing, it may be possible to produce low-cost nanometer composite materials which may prove to be stronger and more durable than the more conventional portland cement-based materials now available. (A6) A

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Microstructure, Porosity and Mechanical Property  
Relations of Calcium-Silicate-Hydrate

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## Microstructure, Porosity and Mechanical Property Relationships of Calcium-Silicate-Hydrate

### Summary of Work

Room temperature hydration studies of Glasses 1-5 (see Figure 1) using TEM have continued for over 200 days. Fragments of each glass have been hydrating in a drop of DI water on TEM grids stored at ~100% relative humidity. Small spherical crystals (10-20 nm) are becoming increasingly more abundant (see Figure 2). These crystals are typical of what is forming in all of the hydration studies. More solid phases are probably present, but they are not crystalline nor well dispersed and therefore difficult to image in this insitu experiment. Electron diffraction patterns of these crystals (see Figure 3) give a 1/4 lattice of wairakite  $[\text{Ca}_8(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}]$ , a calcium analogue of analcime, which is related to the zeolite group. X-ray diffraction patterns of these glasses hydrated with a higher water to solids ratio retain their amorphous character. This suggests either that the hydration products have some short range order, but not enough long range order to diffract x-rays or that the water to solids ratio influences the nature of the hydration products. Work is continuing on these glasses as well as two new glasses (6 and 7) containing additional calcium. See Figure 1 for their composition and location relative to Glasses 1-5.

Similar glass hydration reactions at 90°C have indicated the presence of greater crystallinity in the hydration products, especially in the presence of added alkali. Also, the nature of the hydration products seem to be very sensitive to the bulk chemistry of the starting material. For example, Figure 4 shows a typical microstructure which developed during the hydration of Glass 3 in 0.3M CsOH for more than 90 days. Figure 5 depicts the hydration products of Glass 4, a more silica-rich glass, hydrated under similar conditions. Note that a relatively small change in bulk composition leads to a distinctly different morphology. X-ray diffraction patterns (Figures 6 and 7) and the above SEM photomicrographs suggest that Glass 3 (Figures 4 and 6) consists of calcium silicate hydrate (C-S-H) and Cs-herschelite  $[\text{CsAlSi}_2\text{O}_6 \cdot 3\text{H}_2\text{O}]$  while Glass 4 (Figures 5 and 7) consists of C-S-H plus pollucite  $[\text{CsAlSi}_2\text{O}_6 \cdot x\text{H}_2\text{O}]$ . A hydrothermal experiment in which the Cs-herschelite was treated at 350°C and 4350 psi solution pressure confirmed that the

newly synthesized zeolite was convertible to pollucite, a more traditional Cs-containing zeolite (see Figure 8).

Since the effect of alkali on various bulk chemistries in the system  $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-H}_2\text{O}$  is not well documented, Glass 3 was also exposed to both 0.3M KOH and 0.3M NaOH solutions at 90°C. The microstructure of the hydration products which formed varied as a function of the alkali ion present. Compare Figure 9 (KOH and NaOH hydrated glasses) with Figure 4. Once again these materials are thought to be zeolitic in nature and as can be seen from Figure 9 may also coexist with C-S-H (reticulated phase).

These results as well as those reported earlier (PSU-AFOSR-88-1) suggest that phases present at room temperature should be similar to those found at 90°C except much less crystalline, possibly entirely amorphous. Work following the room temperature hydration of Glasses 3 and 4, and the newly synthesized Glass 6 has begun. See Figure 1 for their location. Work with deionized water and 0.3M NaOH and KOH solutions have resulted in the observation that Glass 6 was most reactive with deionized water producing both crystalline strätlingite [ $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot8\text{H}_2\text{O}$ ] and hydrogarnet [ $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot6\text{H}_2\text{O}$ ]. The addition of alkali apparently retarded the reaction, rather than accelerated it as was the case for the more silica-rich glasses reported earlier (PSU-AFOSR-88-1). All other samples (Glasses GL3 and GL4) have reacted somewhat, but for the most part remain amorphous to x-rays. For these samples, we are also using IR spectroscopy to track the hydration process.

These results once again strengthen our belief that bulk composition and phase chemistry play a major role in determining the microstructure of a given hydrated material which in turn dictates the intrinsic properties of the material. We are presently in the midst of a study of the bounding binary systems  $\text{CaO}\text{-}\text{SiO}_2\text{-H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-H}_2\text{O}$  and  $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-H}_2\text{O}$  using Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS NMR) as a way of delineating phase space for amorphous gel-like materials. A paper dealing with the system  $\text{CaO}\text{-}\text{SiO}_2\text{-H}_2\text{O}$  in which we were able to use a combination of phase equilibria, pH and MAS NMR to delineate the various phases and phase spaces in this system has been accepted for publication by the Journal of the American Ceramic Society. A copy of the paper is appended. An example of a

nanometer composite present in the system is given in Figure 10 which shows two gel-like phases (silica and C-S-H) intergrown as the nanometer scale (mixture A7 in the paper).

#### Future Work

We propose to continue our current studies and also use MAS NMR in conjunction with IR spectroscopy, SEM, x-ray diffraction, etc., to study the bounding ternary systems as well as the larger system (CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O) with and without alkali. If we can delineate phase space, we should be able to begin to engineer the intergrowth of phases i.e. microstructure and porosity to our advantage. Nanometer composite materials in this system may prove stronger and more durable than the conventional portland cement-based materials (macrodefect-free cements, concretes) now available.

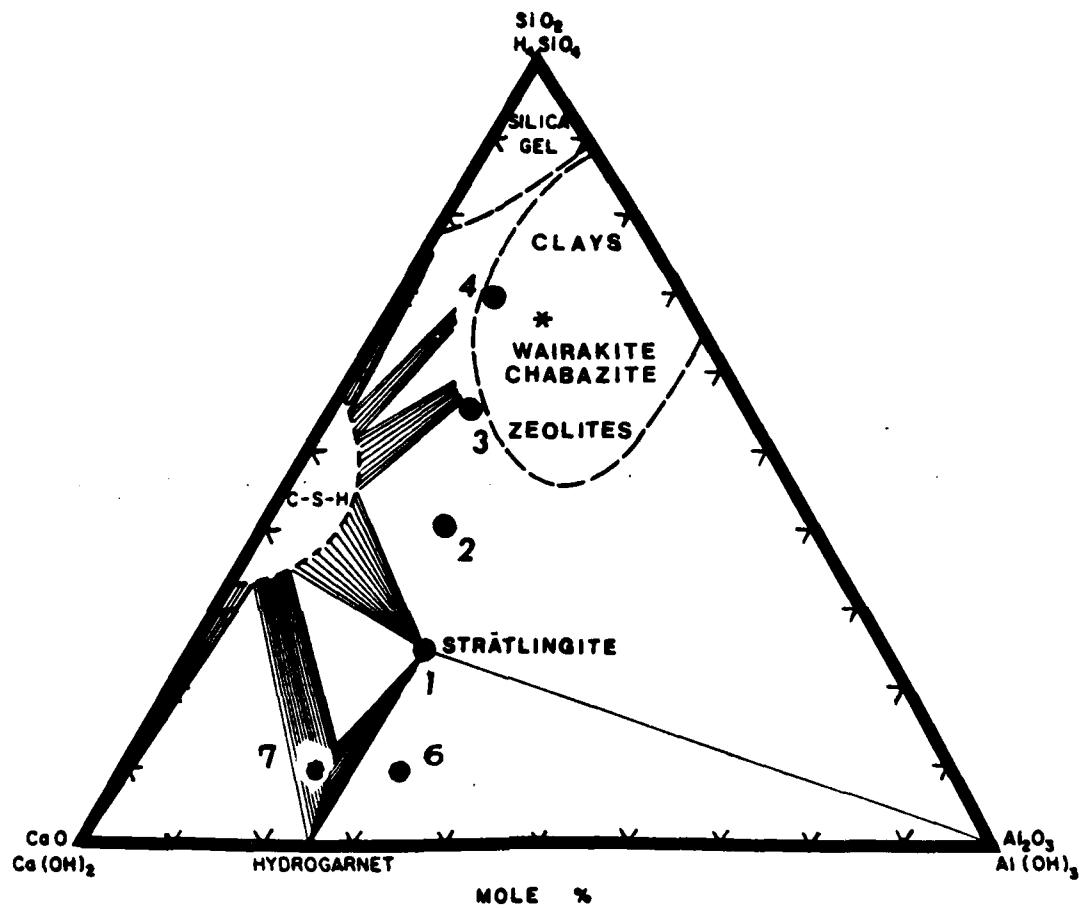


Figure 1. A schematic representation of possible phase relations in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  projected onto the anhydrous base. It is believed that under certain circumstances calcium silicate hydrate (C-S-H), the major cementing material commonly associated with portland cement, can coexist with other amorphous materials (such as a zeolites and/or clays). The glasses under study are indicated on the figure and can be seen to intercept some of these two or three phase areas.

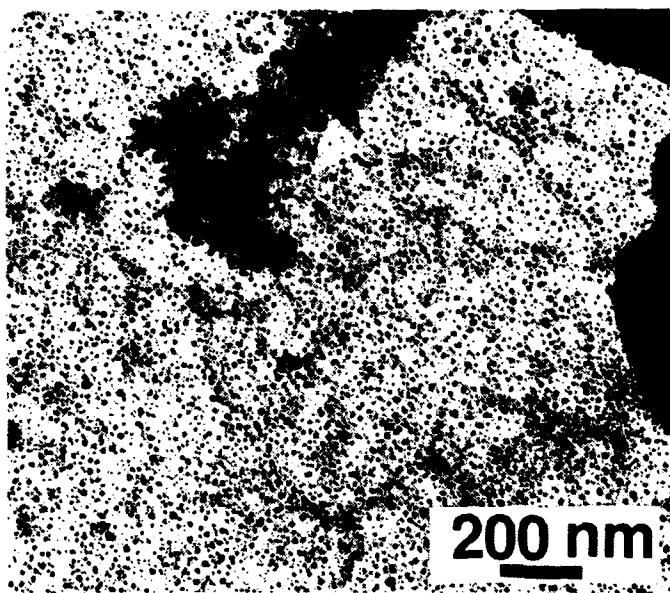


Figure 2. TEM of typical hydration products after 200 days of hydration. The photo shows an example of the nearly spherical grains which become increasingly abundant as hydration proceeds. The shadow to the right is a glass fragment. The crystals are comparatively large (~10 to 50 nm) and give a diffraction pattern of a wairakite with a sublattice 1/4 of that of wairakite.

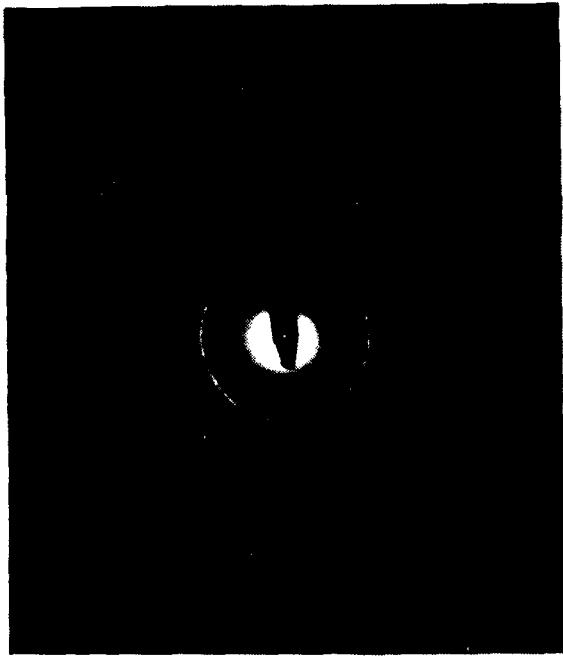


Figure 3. Electron diffraction pattern of spherical crystals.

ring <u>d(A)</u>	pattern (hkl, 1/4 wairakite cell)
2.105	{111}
1.79	{200}
1.28	{220}
1.1	{311}

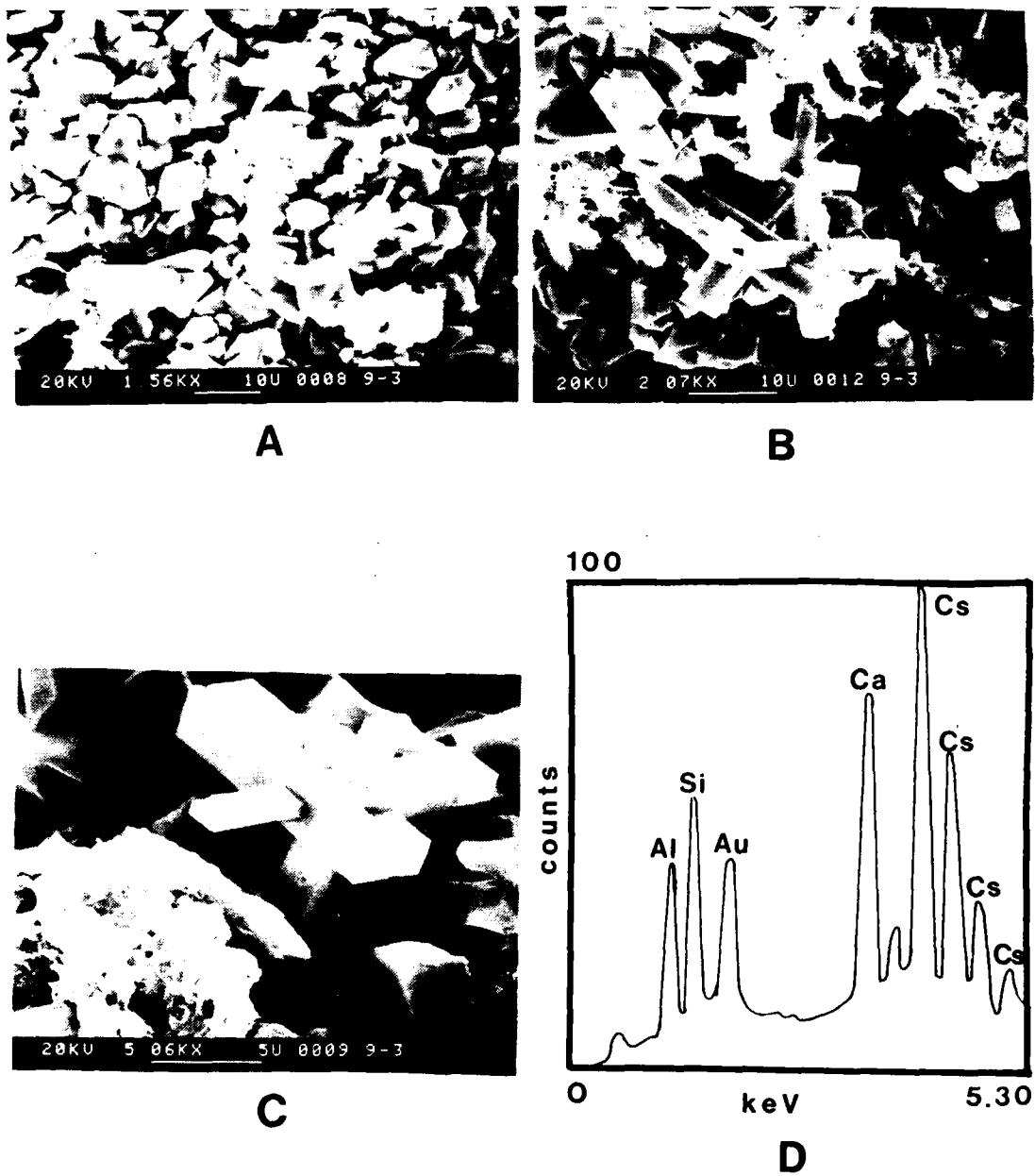
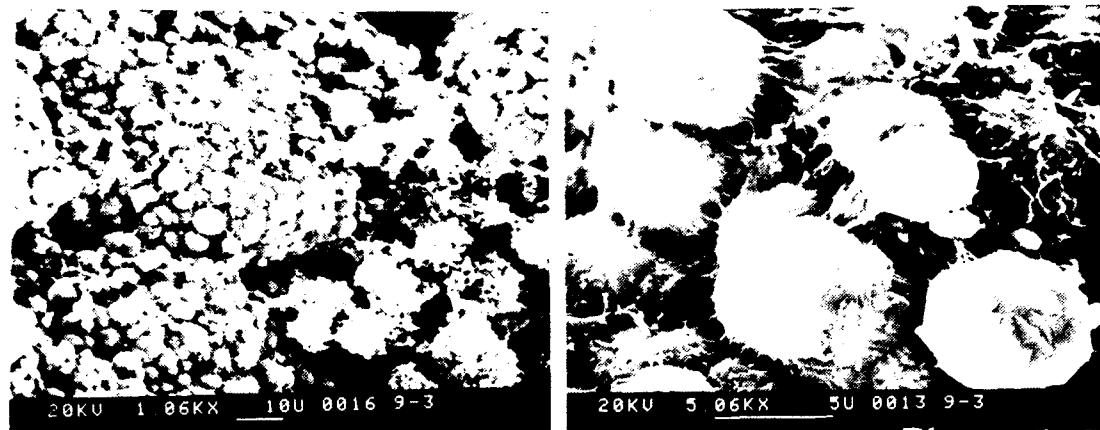
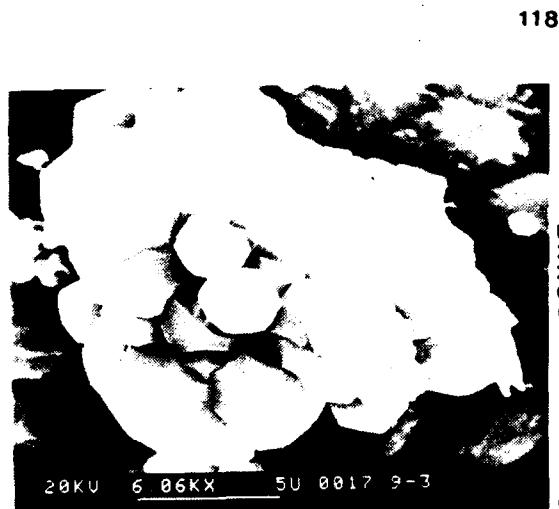


Figure 4. SEM photomicrograph (A-C) and EDAX (D) spectra of Glass 3 hydrated with CsOH solution at 90°C for more than 90 days. The blocky phase is Cs-herschelite, the reticulated phase is C-S-H gel, and the other phases are zeolitic phases which exist in insufficient quantities to identify by X-ray diffraction.

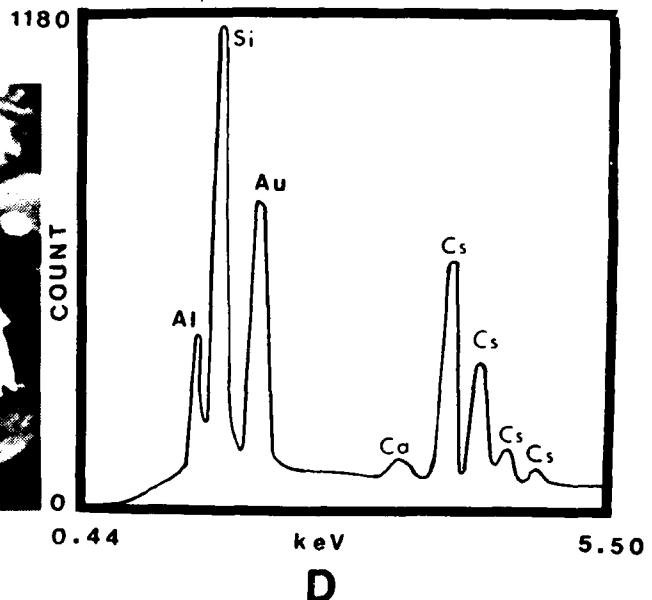


A

B



C



D

Figure 5. SEM photomicrograph (A-C) and EDAX spectra (D) of Glass 4 hydrated with CsOH solution at 90°C for more than 90 days. The polyhedral phase has been identified as pollucite which is coexisting with a reticulated C-S-H gel phase. The C-S-H phase appears to be cementing the pollucite crystals together

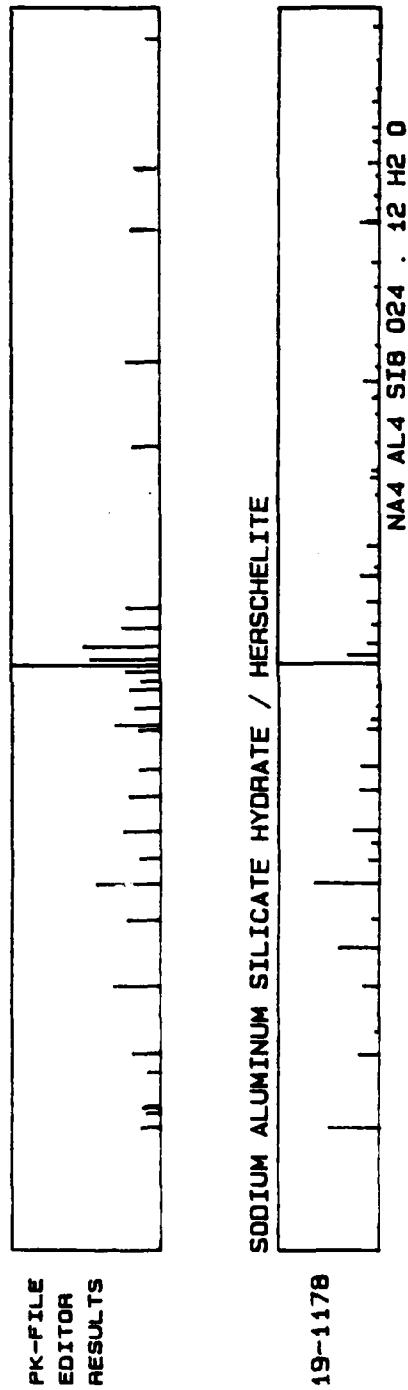
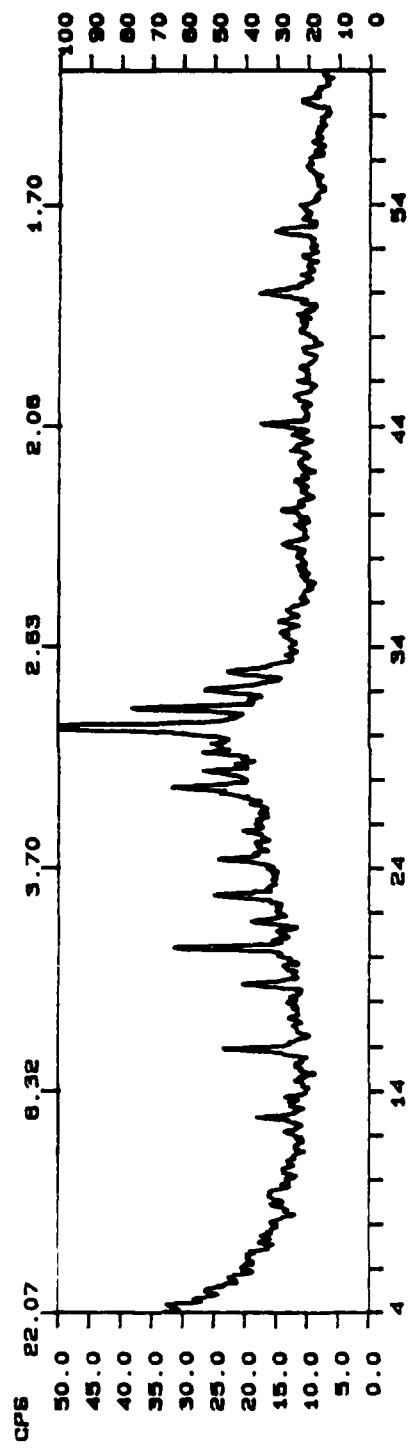


Figure 6. X-ray diffraction pattern for Glass 3 hydrated with CsOH solution at 90°C with a w/s ratio of 10/1 for more than 90 days.

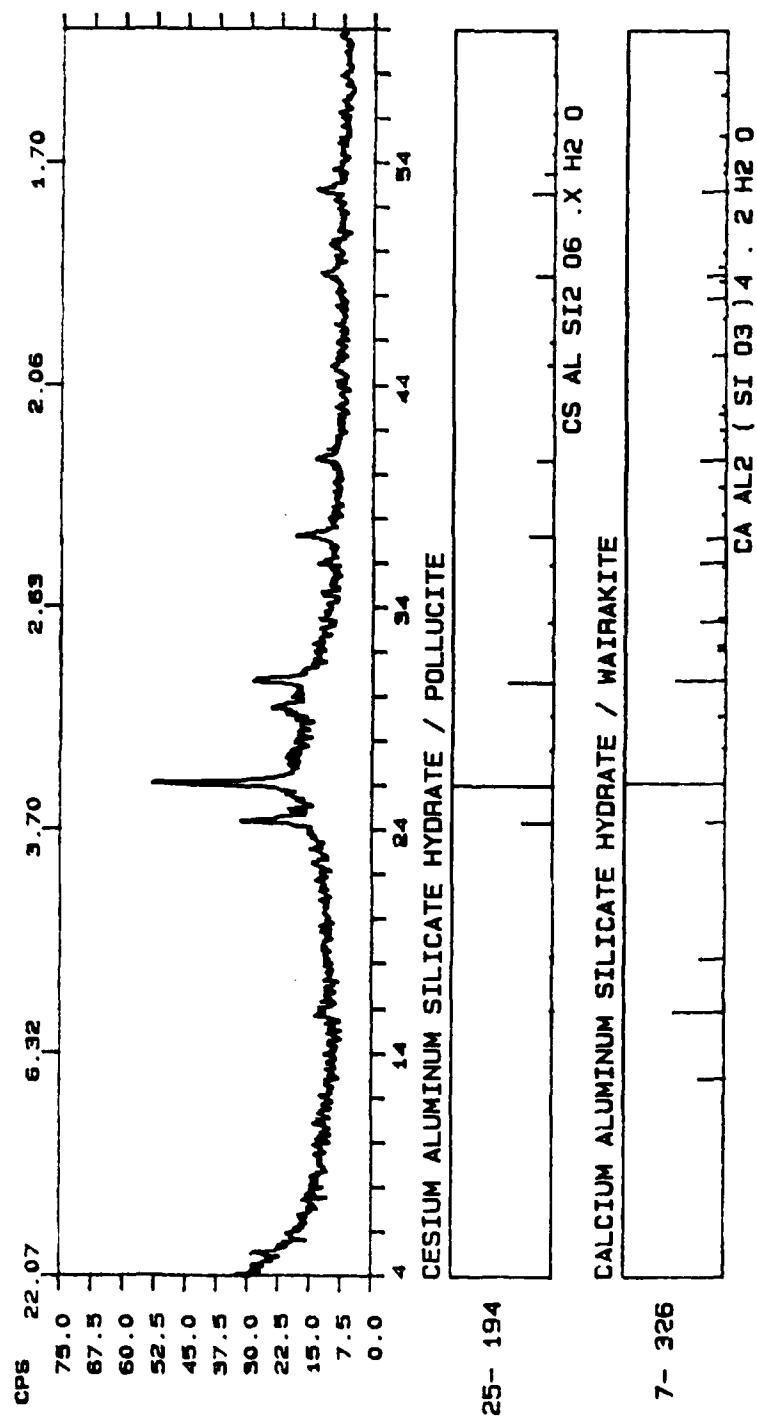


Figure 7. X-ray diffraction pattern for Glass 4 hydrated with CsOH solution at 90°C with a w/s ratio of 10/1 for more than 90 days.

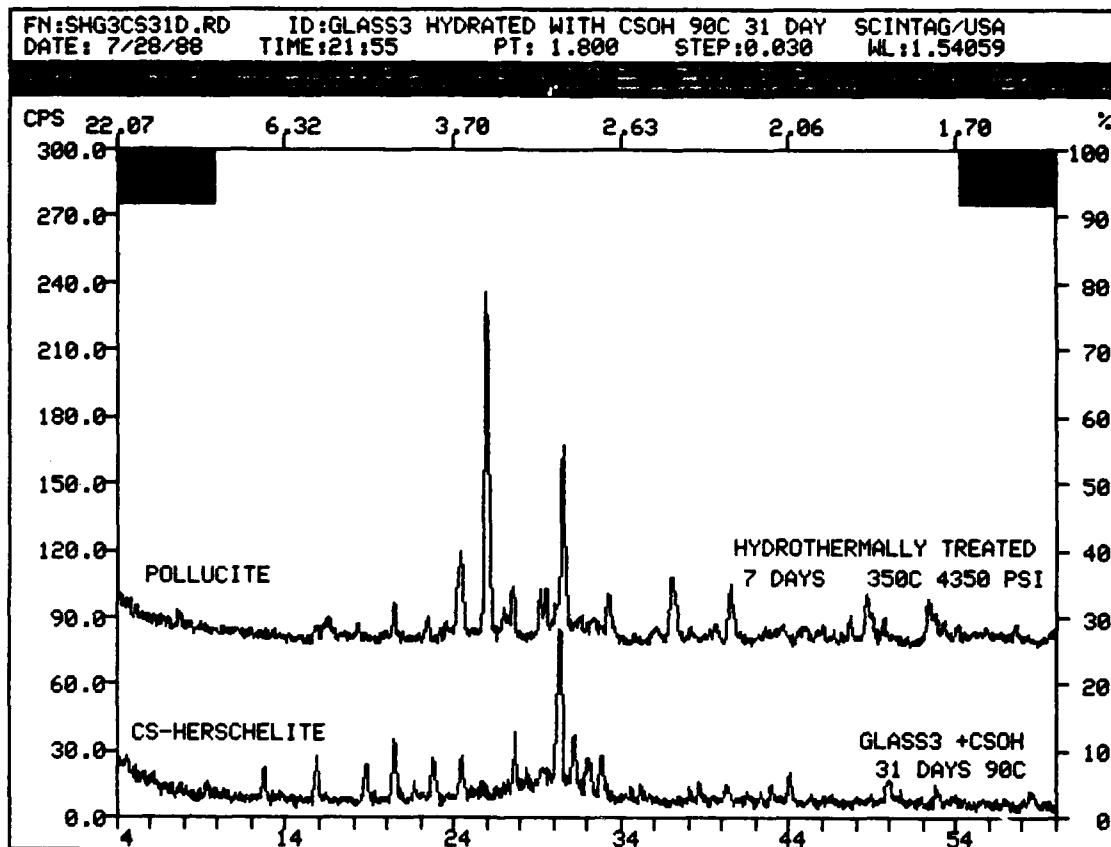


Figure 8. An overlay of originally synthesized Cs-herschelite and hydrothermally produced pollucite. This transformation confirms that the original material was a cesium substituted herschelite.

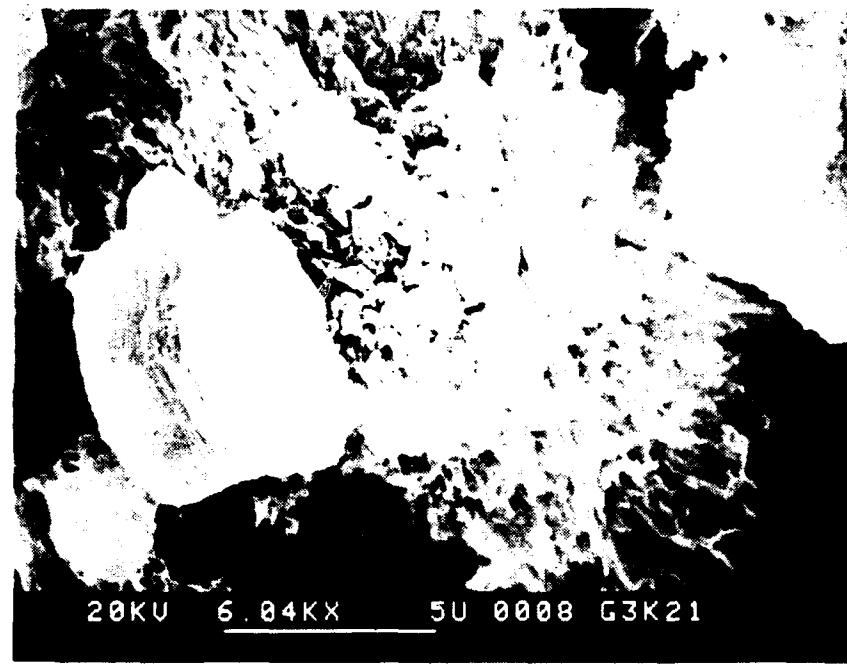


Figure 9. Microstructure of the hydration products of Glass 3 as a function of alkali cation (KOH top photo, NaOH bottom photo).

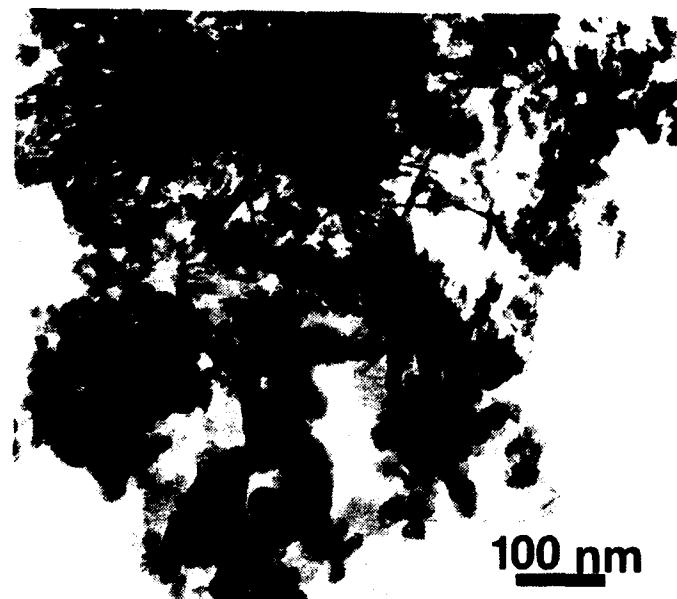


Figure 10. Mixture A7 consists of nanometer-sized equidimensional particles of hydrous silica and fibrous C-S-H which coexist at equilibrium.

**<sup>29</sup>Si MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE STUDY  
OF CALCIUM SILICATE HYDRATE**

**BY**

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## ABSTRACT

$^{29}\text{Si}$  Magic Angle Spinning Nuclear Magnetic Resonance Spectra for the reaction products formed in a series of fully "equilibrated" fumed colloid silica plus lime water mixtures have been recorded. The data suggest that two structurally distinct calcium-silicate-hydrate (C-S-H) phases exist in the system  $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ . The silica-rich C-S-H ( $0.65 < \text{Ca/Si} \leq 1.0$ ) consists predominantly of long chains of silica tetrahedra ( $Q_2$  middle units) similar to those found in 1.4 mm tobermorite. The lime-rich C-S-H ( $\text{Ca/Si } 1.1-1.3$ ) consists of a mixture of dimer ( $Q_1$ ) and shorter chains ( $Q_1$  end units and  $Q_2$  middle units) similar to those found in jennite.

Calcium silicate hydrate (C-S-H), which forms during the hydration of the calcium silicates present in Portland cement, is an amorphous material which is difficult to characterize. Although considerable information is available concerning the physical and chemical properties of C-S-H, its structure is still controversial. When tricalcium silicate is mixed with water, the C-S-H which forms consists of nanometer thick, micrometer-sized foils which intergrow and densify during hydration.<sup>1</sup> It is generally accepted that the silicate anions (tetrahedra) present in C-S-H are polymerized, and that their degree of polymerization increases with time.<sup>2-4</sup> Taylor<sup>5</sup> has suggested that C-S-H consists of disordered layers of short-range order materials with structures similar to those of jennite and 1.4nm tobermorite.

Recently, Lippmaa et al.<sup>6</sup> demonstrated that <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (MAS NMR) could be used to study the connectivity of the silica tetrahedra found in crystalline silicates. Using this technique, "normal" 1.4 nm tobermorite was found to consist predominantly of middle units ( $Q_2$ ) representative of chains of silica tetrahedra,<sup>7-9</sup> and jennite was found to contain both dimer and/or end units ( $Q_1$ ) as well as middle units ( $Q_2$ ).<sup>9</sup>

Since MAS NMR deals with structure on the nanometer scale, the technique is equally well suited to monitor the development of amorphous C-S-H during the hydration of tricalcium silicate. Barnes et al.,<sup>10</sup> have shown that hydration begins with the production of the relatively simple monomeric hydrate ( $Q_0$ ) which tends to persist followed at later stages by a combination of

dimer and/or end units ( $Q_1$ ), and middle units ( $Q_2$ ) which become increasingly abundant with time of hydration. An earlier study by Lippmaa et al.<sup>11</sup> and a more recent work by Young<sup>12</sup> also using MAS NMR to follow the kinetics of hydration of tricalcium silicate have shown that no significant monomer develops during the hydration reaction. Both of these studies show an early development of dimer ( $Q_1$ ) followed by the development of middle units ( $Q_2$ ) after approximately 15 hours of reaction.

Stade and Wieker<sup>13</sup> studied solution precipitated C-S-H using both molybdate and MAS NMR. They found that C-S-H (Ca/Si=1.3) precipitated at 0°C consisted primarially of monomer which quickly condensed to disilicate anions ( $Q_1$ ) with lesser amounts of polysilicate anions ( $Q_2$ ) forming with time. In companion papers<sup>14,15</sup> describing both 80° and 150°C material, Stade and his coworkers suggested that the structure of C-S-H with Ca/Si>1.1 consisted of a fixed ratio (1.2) of polysilicate ( $Q_2$ ) to disilicate anions ( $Q_1$ ), while materials with a Ca/Si ratio  $\leq 1.0$  tended to be richer in polysilicate ( $Q_1$ ).

In related studies, Hara and Inoue<sup>16,17</sup> described the nature of the phases which formed when fumed colloidal silica was allowed to react with 80°C  $\text{Ca}(\text{OH})_2$  solutions. The observed that 1.4 nm tobermorite formed at  $\text{Ca/Si} \leq 0.9$  and jennite at  $\text{Ca/Si} 1.1-1.5$ , reinforcing Stade and coworkers' observation of a structural change at  $\text{Ca/Si} \approx 1.0$ .

The objective of the present study was to use MAS NMR to systematically investigate the structure of the various hydrated phases present at equilibrium in the system  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ . The study was carried out in part to verify whether-or-not silica

sol-Ca(OH)<sub>2</sub> derived C-S-H consisted of a single phase or possibly two phases, and in part to determine if structural data obtained for fully "equilibrated" C-S-H could be used to interpret existing <sup>29</sup>Si MAS NMR data. Our results suggest that two structurally distinct C-S-H phases exist in the system CaO-SiO<sub>2</sub>-H<sub>2</sub>O at pH 11.9. The silica-rich C-S-H (0.65<Ca/Si<1.0) consists predominantly of tobermorite-like middle units (Q<sub>2</sub>), whereas the lime-rich C-S-H (Ca/Si 1.1-1.3) consists of a mixture of both dimer and/or end groups (Q<sub>1</sub>), and middle units (Q<sub>2</sub>) similar to those found in jennite.. No evidence of monomer (Q<sub>0</sub>) was observed.

#### EXPERIMENTAL METHOD

Samples were prepared by combining varying amounts of fumed colloidal silica\*, freshly calcined reagent grade CaCO<sub>3</sub> and freshly boiled deionized water. The compositions that were studied are given in Table 1. Mixtures A1-A11 had a water/solid (W/S) ratio of 11.25 by weight whereas Mixtures B1-B15 had a W/S ratio of 200. The mixtures were allowed to hydrate at room temperature in sealed polyethylene bottles. They were monitored periodically for changes in pH with a Ross pH electrode and an Orion 611 pH meter for one and two years, respectively. The A Mixtures became highly viscous with time making the measurement of pH difficult, therefore to facilitate the measurement, a second set of mixtures were formulated (B Mixtures) having the higher W/S ratio. pH was measured for two reasons, first to track

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\*Cab-O-Sil, Cabot Corporation's fumed silica.

the mixtures' approach to equilibrium and second to delineate phase fields in the system CaO-SiO<sub>2</sub>-H<sub>2</sub>O. The measurement of pH as a function of time suggested that the mixtures approached "equilibrium" relatively rapidly since the pH values did not change to any appreciable extent ( $\pm 0.1$ ) after a month of hydration. Solution analyses were carried out using conventional emission spectroscopy.

Solid material for the MAS NMR study was separated from the solutions by centrifuging them for approximately 10 minutes. The liquid over all samples except Mixture A1 was perfectly clear and easily decanted from the hydrated phases. After saving a small portion of each of the wet solids for SEM examination, the remainder of the solid was freeze dried.

MAS NMR spectra of the freeze-dried samples were obtained at ambient temperature without decoupling or cross polarization on a Chemagnetics CMC-300A NMR spectrometer operating at 59.17 MHz for <sup>29</sup>Si. Samples were spun at ~3kHz. Chemical shifts were obtained relative to tetramethylsilane (TMS) by setting the transmitter frequency on-resonance for a separate sample of TMS, and then measuring offsets relative to this frequency. All spectra were obtained with a pulselength of 4  $\mu$ sec (~75° pulse), a relaxation delay of 11 sec, and four dummy pulses to achieve steady state magnetization. The number of transients collected was typically 1000-9000.

An ISI DS-130 scanning electron microscope was used to examine the microstructure of the hydrated phases and to check for carbonation. No trace of calcite was observed in any of the A Mixtures. The B mixtures were not examined with the SEM.

## RESULTS

The bulk compositions of the mixtures fall in various phase fields consisting of hydrated solid(s) and coexisting solution. Since the system is ternary and temperature and pressure are fixed, whenever two solid phases coexist with liquid, the system is by definition invariant. The two invariant triangles in the system contain: hydrous silica + C-S-H + solution, and C-S-H +  $\text{Ca}(\text{OH})_2$  + solution. Compositions falling within the boundaries of these triangles consist of various proportions of the end-member phases whose compositions are fixed. Therefore the systematic measurement of a solution variable such as pH as a function of the Ca/Si molar ratio of the solid (Ca/Si) would necessarily delineate the position of these invariances.

A plot of Ca/Si of the solid versus pH obtained for the A and B series of mixtures is given in Figure 1. An invariance is indicated by the vertical portion of the curve at pH 9.9 which extends from Ca/Si approximately 0.05 to 0.65. Over this interval, phases coexisting with solution are hydrous silica containing a few mole percent calcium oxide and C-S-H with a Ca/Si ratio of approximately 0.65. As the system becomes richer in calcium, i.e.  $\text{Ca/Si} > 0.65$ , only the single solid phase, C-S-H, coexists with solution, the system is no longer invariant and the pH is seen to rise. The curve is similar in form to the many "equilibrium" Ca/Si versus Ca curves in the literature, e.g. Steinour.<sup>18</sup> In fact, chemical analyses of the B mixture solutions after nine weeks (Table 1) showed that they fell on these same curves, indicating that "equilibrium" had indeed been achieved.

However, if two C-S-H phases were to coexist, the system would once again become invariant. The curve for C-S-H which is given in Figure 1 may in fact contain such a small two-phase region at pH 11.9 where two C-S-H phases having Ca/Si ratios of 1.02 and 1.06 could coexist with solution.

The measured  $^{29}\text{Si}$  MAS NMR chemical shifts for six key samples (numbered samples in Fig. 1) as a function of their Ca/Si ratio are given in Table 2. To aid the discussion, the accompanying spectrum for each sample has also been plotted as well as an insert showing the MASNMR spectra for tobermorite and jennite (see Fig. 2). The spectrum for hydrous silica (Ca/Si=0.02) is similiar to those given in the literature.<sup>19</sup> The peaks at -100.7 and -114.5 ppm are attributed to  $\text{HOSi(OSi)}_3$  and  $\text{Si(OSi)}_4$ , respectively which are characteristic of tertiary (Q3) and quaternary (Q4) networks of silica tetrahedra<sup>6</sup> found in silica gel. Apparently the addition of 2 mol % CaO to silica gel does not alter its structure to any significant extent. The spectrum of the invariant sample with Ca/Si=0.12 (hydrous silica + C-S-H + solution) consists of peaks representing the same silica gel (-100.7, -114.7 ppm) and an additional peak at -85.0 ppm. The new peak is characteristic of secondary (Q<sub>2</sub>) unbranched chains of silica tetrahedra.<sup>6</sup> The spectra for mixtures with Ca/Si=0.71 and 0.91 (single phase C-S-H), contain a similar Q<sub>2</sub> peak at -85.0 and -86.8 ppm, respectively. Although the chains are relatively long, there is a suggestion that they become shorter with increasing Ca content of the mixtures since a small shoulder attributable to end groups (Q1) can be seen in the Ca/Si=0.91 sample. The spectrum for the sample with Ca/Si=1.07, which has a

pH of approximately 12, contains two peaks: a peak at -85.8 ppm which is again attributed to  $Q_2$  middle units and an additional peak at -79.2 ppm. This new peak corresponds to dimer and/or end unit silica tetrahedra ( $Q_1$ ).<sup>6</sup> The final sample (Ca/Si=1.31), whose spectrum matches that of the Ca/Si=1.07 sample, also contains  $Q_1$  and  $Q_2$  peaks at -86.6 and -80.4 ppm, respectively.

In addition to the MASNMR data given above, which indicate structural differences in the C-S-H, the consistency of the W/S = 11.25 sample with Ca/Si=1.07 was noticeably "thicker" and the microstructure more "foil-like" than the companion sample with Ca/Si=0.71, and unlike samples having Ca/Si ratios of 0.02, 0.12, and 0.71, contained no standing water.

#### DISCUSSION

The reported MAS NMR spectra as well as the shape of the C-S-H portion of the Ca/Si versus pH curve obtained during the present study, confirm that, at equilibrium, two structurally distinct C-S-H phases do in fact exist in the system CaO-SiO<sub>2</sub>-H<sub>2</sub>O at pH 11.9. See Figure 3 for a "not impossible" schematic representation of the proposed two C-S-H system. The spectra of the silica-rich C-S-H ( $0.65 < \text{Ca/Si} \leq 1.0$ ) given in Figure 2 are dominated by a single  $Q_2$  peak which represents chains of silica tetrahedra similar to those found in "normal" 1.4 nm tobermorite.<sup>7,9</sup> These observations parallel the findings of Stade and his coworkers<sup>13-15</sup> as well as Hara and Inoue<sup>16,17</sup> who observed an increasing tendency to form polysilicate and tobermorite, respectively, in their low Ca/Si ratio C-S-H precipitates.

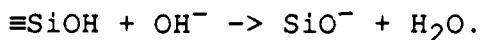
MORE

The spectra of the lime-rich C-S-H ( $\text{Ca/Si} \geq 1.1-1.3$ ) obtained during the present study consist of two peaks having, what appears to be, a fixed  $Q_2/Q_1$  peak height ratio of 0.7. These results suggest that the lime-rich C-S-H is dominated by dimer and/or end groups ( $Q_1$ ) and to a lesser extent chains of silica tetrahedra ( $Q_2$ ), and that the structure of this C-S-H is relatively insensitive to changes in composition. The spectra for the lime-rich C-S-H recorded during this study are similar to that reported for 80°C synthetic jennite,<sup>9</sup> although jennite's  $Q_2/Q_1$  ratio of 1.5 is somewhat larger. Once again, these results parallel those reported by Stade and his coworkers<sup>14,15</sup> in as much as they also report a similar tendency of their lime-rich C-S-H to contain both polysilicate and disilicate anions having a fixed ratio of 1.2. Finally, Hara and Inoue successfully synthesized jennite only when their Ca/Si ratio exceeded 1.1.

The suggestion that two structurally distinct C-S-H phases exist in this system is strengthened, by the fact that the observed transition from the "one peak" to the "two peak" situation is abrupt (<4 mol % CaO separate the spectra) rather than gradual which might be expected if changes were attributable to adsorption or variation in a solid solution series. In addition, the Ca/Si versus pH curve contains a noticeable inflection and possible invariance at a pH of approximately 11.9 which occurs between the two sets of C-S-H spectra. Finally, the existence of two C-S-H phases in the System  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  tends to confirm earlier suggestions of invariance found in the works of Roller and Irvin,<sup>20</sup> Flint and Wells<sup>21</sup> (see

Fig. 4) and Ramachandran<sup>22</sup> which occur at a pH of approximately 11.5.

In toto, the work suggests that two materials having short-range order can coexist at equilibrium, i.e. gel-immiscibility may in fact exist on the nanometer scale in X-ray amorphous materials. However, the nature of the phase separation is still under study. Clearly, the silica-rich C-S-H has a tobermorite-like structure consisting of relatively long chains of silica tetrahedra with little or no contribution from end groups ( $Q_1$ ) except perhaps at its upper stability limit ( $Ca/Si=1.0$ ). The structure of the lime-rich C-S-H is more problematic. Since the  $Q_2/Q_1$  ratio of these materials are very sensitive to synthesis temperature<sup>15</sup> at this point one can only infer that it consists of a mixture of dimer and shorter chains of silica tetrahedra similar to those found in jennite.<sup>9</sup> In addition, if the lime-rich C-S-H has a fixed  $Q_2/Q_1$  ratio, this would imply that the anionic silicate structure remains constant as the Ca/Si ratio changes, which further reinforces the concept of discrete phase formation. Stade et al.<sup>15</sup> has suggested the following mechanism to maintain charge balance in such a situation:



Although it is often "dangerous" to speculate as to the relevance of these results to paste-hydration studies, it is at least interesting to note that the spectra obtained for the lime-rich Mixtures ( $Ca/Si=1.07$  and  $1.31$ ) look identical to similar spectra obtained for long-duration room-temperature paste-hydrated samples of tricalcium silicate and water.<sup>11,12</sup>

Finally, the absence of monomer ( $Q_0$ ) in the equilibrium mixtures studied suggests that monomer may somehow be related to the very early surface attack of tricalcium silicate by water.

#### ACKNOWLEDGEMENTS

We thank C. Schauer and R. Gallager for their help in preparing the mixtures and monitoring their pH and G. W. Wagner for help with MAS NMR measurements. MG thanks NSF-MSM-8304076 and AFOSR- 87-0395 for support. Helpful discussions with H.F.W. Taylor and S. Komarneni are appreciated.

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## FIGURE CAPTIONS

Figure 1. The Ca/Si molar ratio of the solid plotted as a function of the pH of the coexisting solution phase. Two invariancies exist in the system, one at pH 9.9 and one at 11.9.

Figure 2.  $^{29}\text{Si}$  MAS NMR spectra of Mixtures in the System  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ . Chemical shifts are reported relative to TMS. The insert has been adapted from Komarneni et al.<sup>9</sup>

Figure 3. Schematic representation of room temperature phase relations in the System  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ . Whereas the placement of the phase fields for the two C-S-H phases is reasonably accurate (based on present and literature data), for ease of discussion, the corresponding solution compositions have been highly exaggerated.

Figure 4. The Ca/Si molar ratio of the solid versus calculated pH of the coexisting solution phase. The original data of Roller and Irvin<sup>20</sup> and Flint and Wells<sup>21</sup> have been reworked by Ramachandran<sup>22</sup> from which this figure is taken.

Table 1. Composition of Mixtures and Corresponding Fully Equilibrated Solutions.

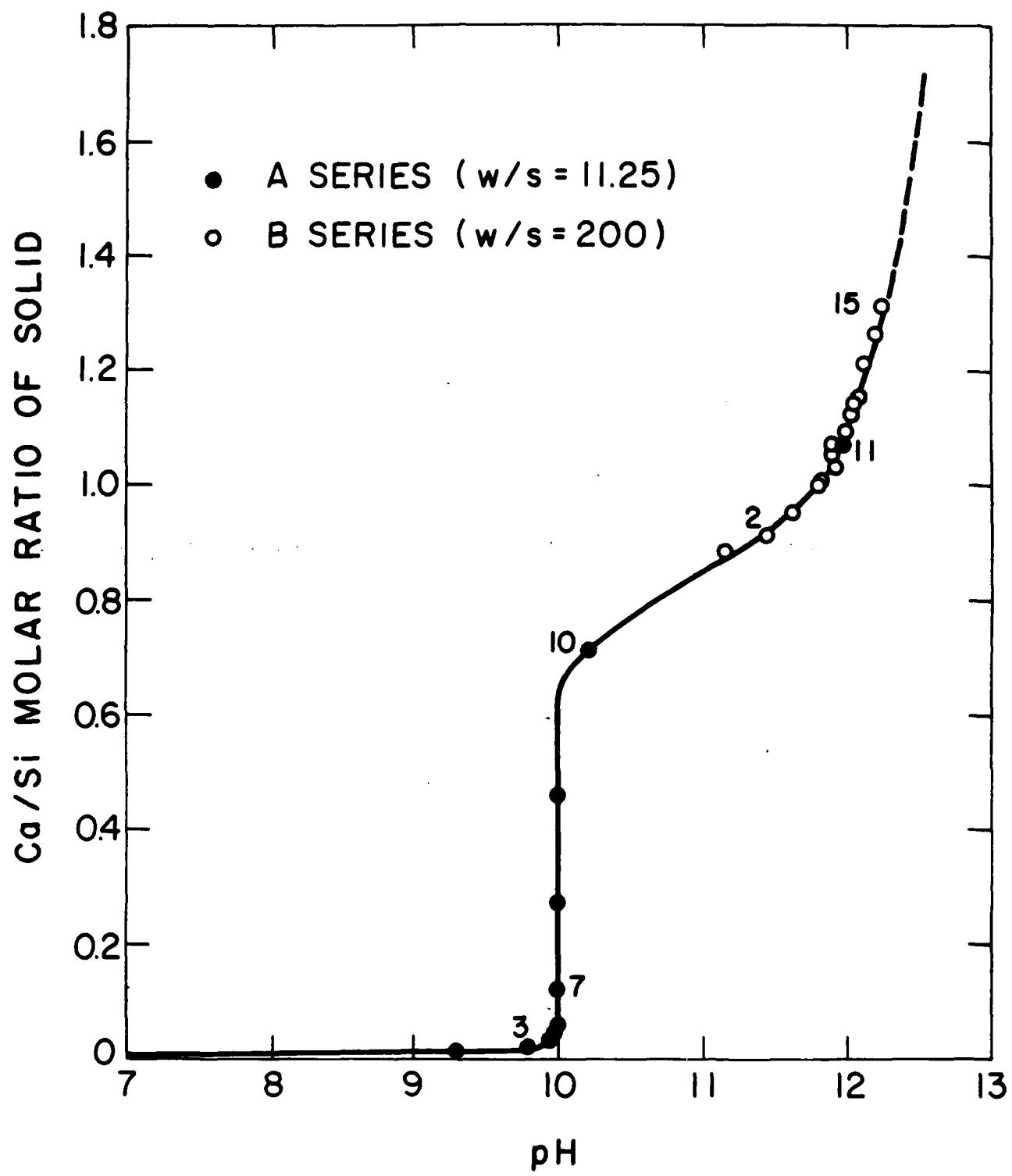
Mixture	CaO mol%	Ca/Si**	pH	Ca mmol L <sup>-1</sup>	Si mmol L <sup>-1</sup>
A1	0	0	4.53	--	--
A2	1.0	0.01	9.30	--	--
A3	2.1	0.02	9.80	--	--
A4	3.2	0.03	9.96	--	--
A5	4.3	0.04	9.98	--	--
A6	5.3	0.06	9.99	--	--
A7	10.6	0.12	9.98	--	--
A8	21.1	0.27	9.97	--	--
A9	31.5	0.46	9.98	--	--
A10	41.7	0.71	10.21	--	--
A11	51.7	1.07	10.21	--	--
B1	46.7	0.88	11.15	1.20	0.82
B2	47.7	0.91	11.44	1.48	0.39
B3	48.7	0.95	11.63	1.90	0.27
B4	49.7	0.99	11.81	2.84	0.19
B5	50.2	1.01	11.82	2.91	0.20
B6	50.7	1.03	11.95	3.89	0.16
B7	51.2	1.05	11.91	3.59	0.17
B8	51.7	1.07	11.90	3.51	0.17
B9	52.2	1.09	12.00	4.49	0.15
B10	52.7	1.12	12.04	4.86	0.14
B11	53.6	1.14	12.06	5.16	0.14
B12	53.7	1.16	12.11	5.98	0.13
B13	54.7	1.21	12.13	5.98	0.13
B14	55.7	1.26	12.20	6.73	0.12
B15	56.7	1.31	12.26	8.23	0.11

\*Anhydrous basis

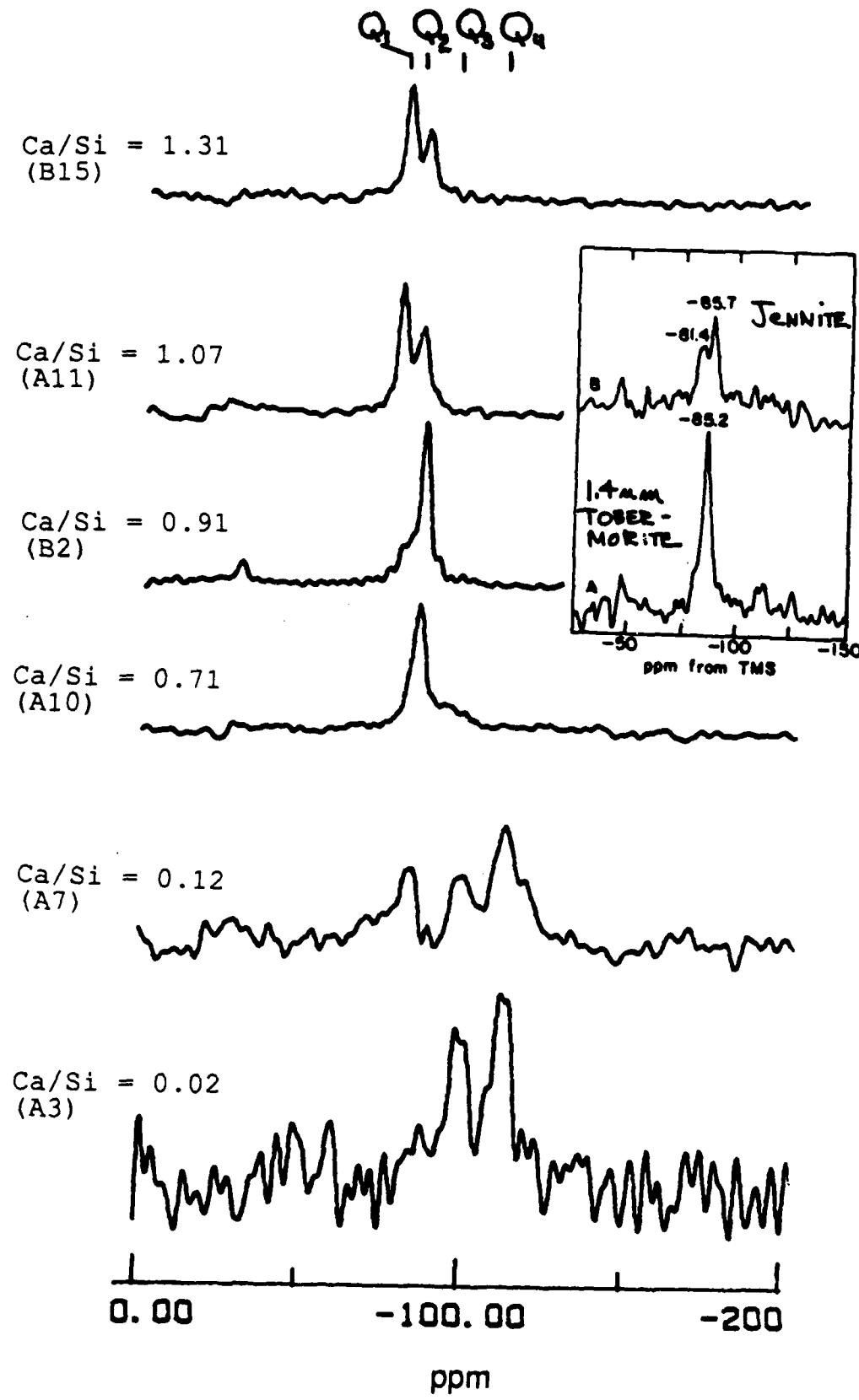
\*\*Molar ratio of solid(s)

Table 2. Observed  $^{29}\text{Si}$  Chemical Shifts as a Function of C/S Ratio of Solids.

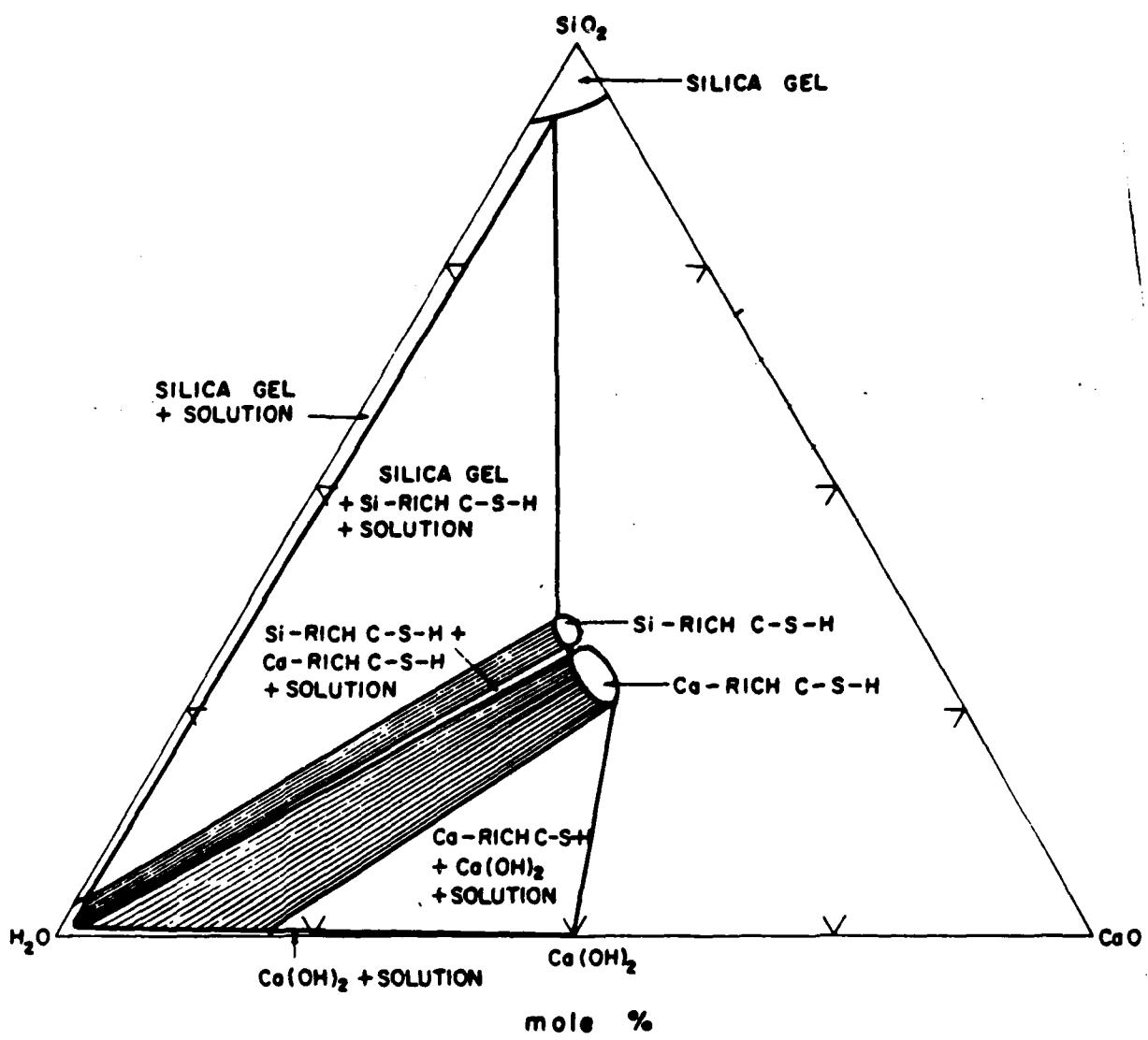
Mixture	C/S	$\text{Q}_0$	$\text{Q}_1$	$\text{Q}_2$	$\text{Q}_3$	$\text{Q}_4$
A3	0.02	--	--	--	-100.7	-114.5
A7	0.12	--	--	-85.0	-100.7	-114.7
A10	0.71	--	--	-85.0	--	--
B2	0.91	--	--	-86.8	--	--
A11	1.07	--	-79.2	-85.8	--	--
B15	1.31	--	-80.4	-86.6	--	--



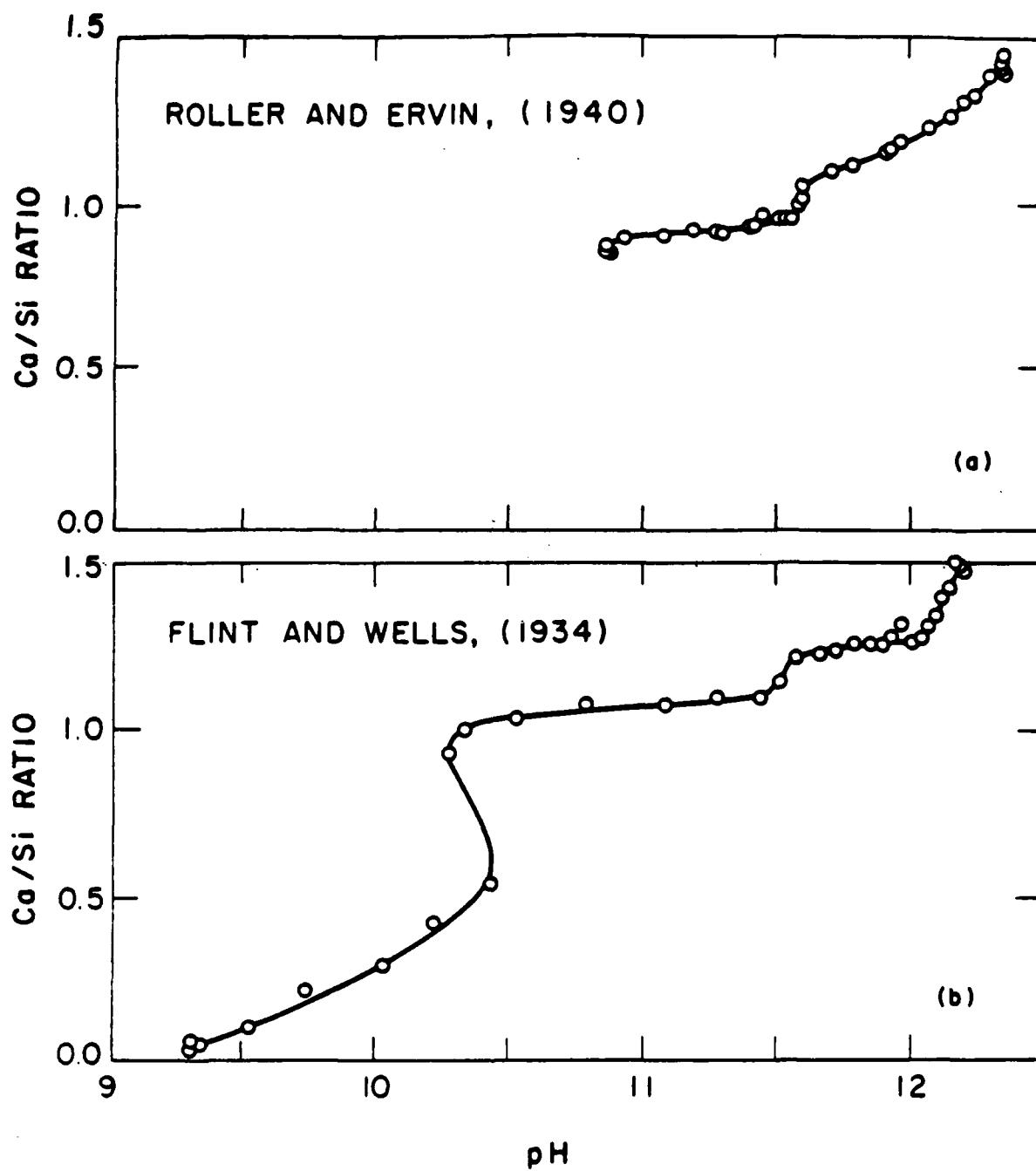
Guttmann et al. Fig. 1



Grutzelk et al. Fig. 2



Grubbe et al. Fig 3



Grubbe et al. Fig 4.